SYNTHESIS, CHARACTERIZATION AND EFFECT OF ATMOSPHERE ON SINTERING BEHAVIOR OF $BaTiO_3$ NANO-POWDERS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
In
Ceramic Engineering

By
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Under the Guidance of
Prof. Debasish Sarkar

Department of Ceramic Engineering
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Rourkela
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National Institute of Technology
Rourkela

CERTIFICATE

This is to certify that this thesis entitled, "SYNTHESIS, CHARACTERIZATION AND EFFECT OF ATMOSPHERE ON SINTERING BEHAVIOR OF $BaTiO_3$ NANO-POWDER", submitted by Mr. Rahul Prakash in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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CONTENTS

ABSTRACT

Barium Titanate ($BaTiO_3$) is a classic perovskite material for the manufacture of multilayer ceramic capacitor (MLCC) in electronic industry. Day to day miniaturization mobile device demands $BaTiO_3$ nanoparticles to fabricate multilayer along with metal electrode and hence control atmosphere sintering is necessary to achieve best performance of this metal-ceramic composite layers. Hence, prime objective of this work was to synthesis of $BaTiO_3$ nanopowders, their relevant characterization and finally their sintering behavior study at different atmospheres at different sintering profile. In this research, combined wet-chemical and subsequent calcination technique has been adapted to synthesis nanoscale $BaTiO_3$ powders. Cosmetic grade TiO_2 was used to prepare $BaTiO_3$ nanoparticles from as-synthesized elongated $BaCO_3$ nanoparticles. Pure, high crystalline, $BaTiO_3$ powder was successfully synthesized at 1100^oC. Powders were consolidate through uniaxial press and sintered in dilatometer furnace at different temperature profile in air, argon and nitrogen atmosphere. Maximum density was obtained in air and lowest in argon atmosphere, this is due to effect of partial pressure of oxygen. A significant change in d-spacing was also observed after control atmosphere sintering at 1250^oC and 1350^oC. The sintering behavior and their microstructure could be modified through synchronization of consolidation technique and gas flow rate.

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Chapter 1

General Introduction

1.1 Introduction to $BaTiO_3$:

Chemical formula: $BaTiO_3$

Compound type: Inorganic

Structure: Perovskite

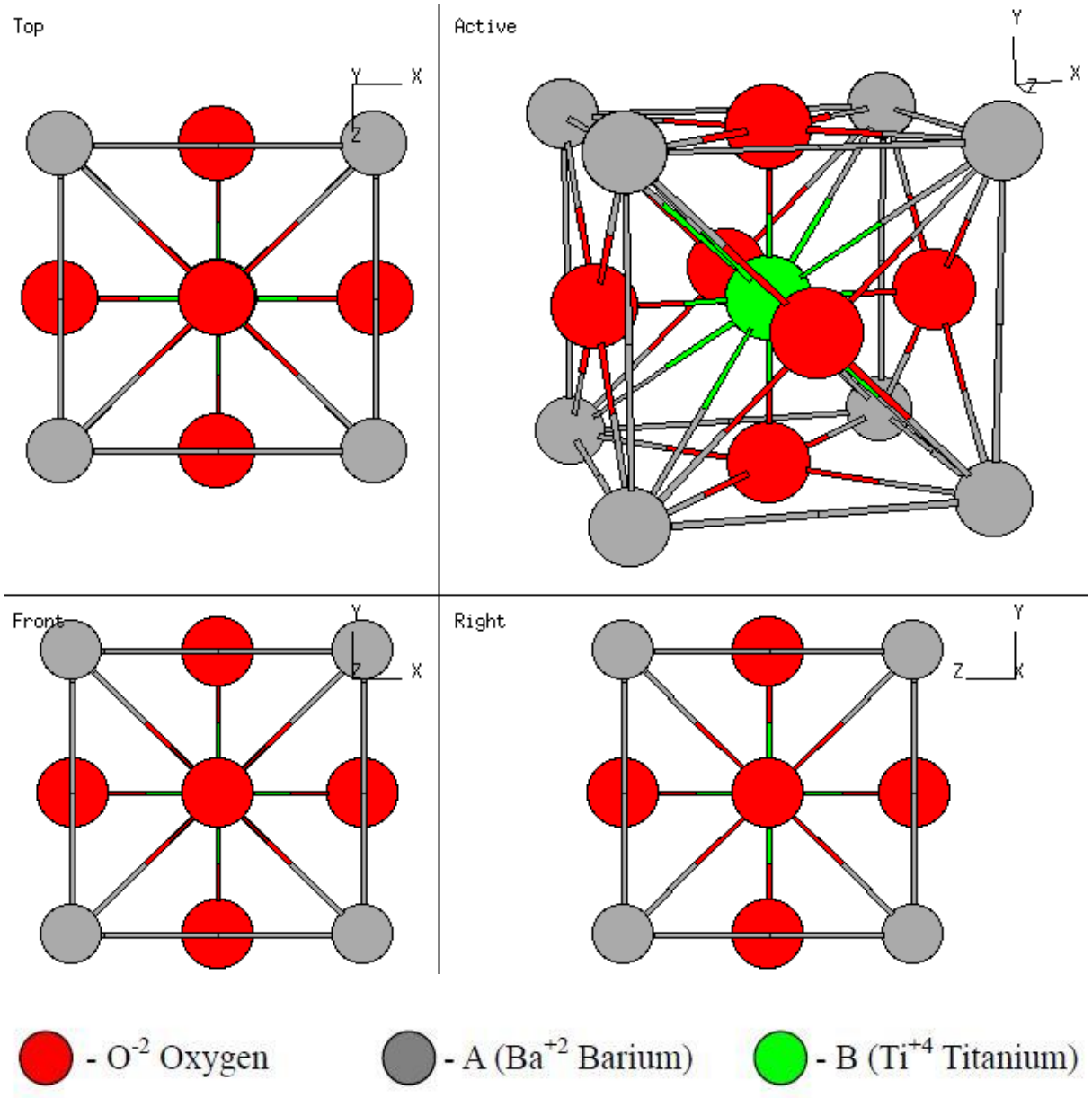


Fig.1.1 Perovskite Structure[1]

$BaTiO_3$: The prototypical Ferroelectric

The observation of ferroelectric behavior in $BaTiO_3$ made it first and probably the most extensively investigated of all ferroelectrics and is basically due to the properties of its polymorphs. The discovery led to the availability of dielectric constant (**κ**) up to 2 orders of magnitude, greater than that had been known before. Reasons that made $BaTiO_3$, a curious field of study:

- Relatively simple crystal structure
- Ferroelectric at room temperature (θ_c=120°C)
- Durable
- Easily prepared in the form of thin film, single crystal, or polycrystalline ceramic [2]

1.2 Crystal Structure:

The Ba^{2+} and O^{2-} forms a face centered cubic arrangement with Ti^{4+} occupying the octahedral interstices. $BaTiO_3$ exhibits para-electricity and an isotropic di-electricity due to the high symmetry of its cubic phase. When cooled below θ_c , there is a change in structure from cubic phase to distorted tetragonal with the displacement of positive and negative charge centers within the sub-lattice[3]. Due to this , a dipole moment parallel to one of the cubic axes of original phase arises and this spontaneous polarization generated in the tetragonal structure leads to piezoelectric and ferroelectric behavior.

Transformations:

Rhombohedral(<-90°C), Orthorhombic(<0°C), Tetragonal(<120°C), Cubic(>120°C)

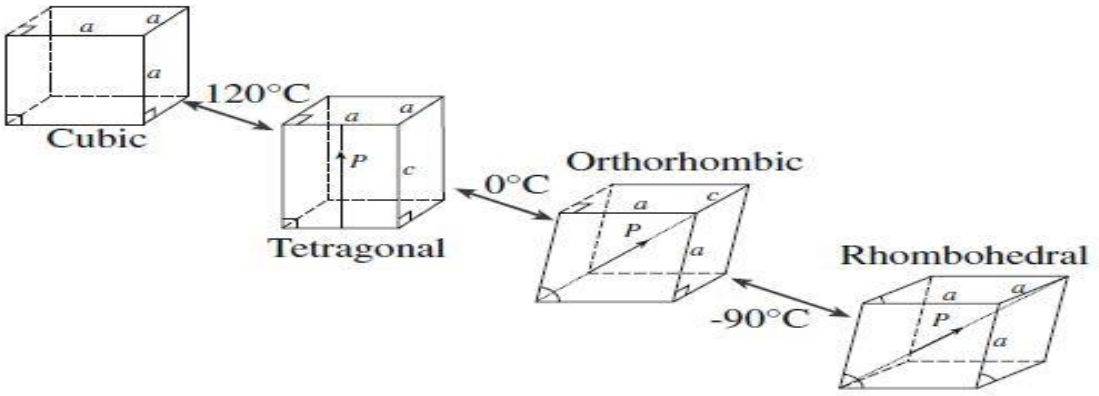


Fig 1.2 $BaTiO_3$ Polymorphs showing direction of polarization [2]

However $BaTiO_3$ is rarely used in its pure form, solid-solution with an iso-structural compound is used to broaden the θ_c as well as shifting it to the lower temperatures.

(Ex: solid solution of $BaTiO_3$ and $SrTiO_3$) [2].

The firing of $BaTiO_3$ ceramics in an inert atmosphere (argon) , without sacrificing densification can lead to a dramatic increase of both the dielectric constant and dissipation factor of the samples[4].

1.3 Properties of $BaTiO_3$:

- Ferroelectric
- By implication ,para-electric and also piezoelectric material
- Hysteresis loop for polycrystalline $BaTiO_3$ ceramic has a higher E_c and lower P_r than the single crystal.
- Melting point is 1625°C.
- Density is 6.02 gm/cc.
- Behaves as Relaxor dielectric, κ and tanδ changes with frequency.

To achieve high values of dielectric constant at room temperature stability over wide range of temperature T [2].

- Solid solution can be formed
- Grain size can be reduced
- Induction of mechanical stresses in thin films

  So study of all these aspects are of great importance to enhance the applicability.

1.4 Applications of $BaTiO_3$:

$BaTiO_3$ being a dielectric ceramic is used for capacitors (Disk capacitors, MLCC etc.). Also as a piezoelectric material it is used for transducers and microphones. The Curie point of $BaTiO_3$ is 120 °C and its spontaneous polarization is about 0.15 C/m^2 at room temperature [5]. Polycrystalline $BaTiO_3$ exhibits positive temperature co-efficient, making it useful for thermistors and self-regulating electric heating systems.

1.5 Major Research on $BaTiO_3$:

The recent advances relating to electronic devices modeled from $BaTiO_3$ show the trend of improved performance with continuous miniaturization. For MLCCs, this means enhanced capacitance per unit volume of the component. This can be achieved by increasing the number of active layers to 200–400 and by lowering the dielectric layer thickness below 2–3μm [6]. For capacitors, important properties such as break down voltage and DC leakage are dependent on the pore defects, layer thickness and grain size. The effective thickness of dielectric layer is expected to be several, e.g. at least 3–5, grains. Therefore $BaTiO_3$ powders with particle size in nanometer- range, a large surface area with high homogeneity are required to achieve good sinterability as well as fine grained microstructure in sintered ceramics.

1.6 Outline of the Report:

A brief introduction to the topic in hand is presented, has been displayed in this chapter. The next chapter covers the available literature, and towards the end of the chapter, is discussed the objectives and motivation of our work. Chapter 3 describes in detail the experimental methods and the characterization techniques employed during the research work. Chapter 4 discusses the results obtained, and seeks to provide an explanation to those results. The conclusions of the work are summarized in the final chapter, and along with it, is provided some hints to future work.

Chapter 2

Literature Review

2.1 Synthesis of $BaTiO_3$ nano-powders.

Different chemical methods have been established for the preparation of cubic and/or tetragonal $BaTiO_3$ nano-powders. The wet chemical process, carried out at room temperature, dominated to the formation of 30nm para-electric cubic phase. Hence, subsequent post-heat treatment is required to get tetragonal phase in $BaTiO_3$ powder; however increase in the particle size has been observed which is beyond the objective [7-9]. On the other hand, the hydrothermal method can be employed to synthesize < 100nm tetragonal **$BaTiO_3$** nano-powders, but process is expensive and intra-particle porosity deteriorates the property [10-11].

D. Sarkar et. al [12] proposed a new combined technique for the preparation of pure, non-porous, near spherical and high c/a ratio(>1.009) of 125 nm grade tetragonal $BaTiO_3$ nano-powders. The technique involved wet-chemical method for the synthesis of powder precursor ($BaCO_3$+TiO_2) and for the calcination of dry precursor rapid heating (20°C/min.) and isothermal treatment at 1100°C was done followed by quenching of the calcined powder from 1100°C to 5°C in ~5 secs. Rapid cooling resulted into increment of c/a ratio and also it was observed that cooling below 5°C diminishes c/a ratio, presumably due to temperature dependent polymorphic transformation.

Buscaglia et. al.[13] reported a low temperature(700-800°C) synthesis method for the 70-85nm $BaTiO_3$ nano-powders with $BaCO_3$+TiO_2 precursors as starting materials. The particle size obtained was much lower but the c/a ratio was lower than that reported by D. Sarkar et. al[12].

2.2 Sintering of green specimen of $BaTiO_3$ nano-powders in inert/reducing atmosphere.

The interest in sintering of green specimen of $BaTiO_3$ nano-powders in inert / reducing atmosphere, is gaining popularity with an objective to reduce the cost of MLCC'S by developing $BaTiO_3$ based composition that can be sintered in inert/reducing atmospheres so that the use of cheap base metal (e.g., nickel) electrodes could be possible. To modify the variation of capacitance with temperature, generally, additives like Bi_2O_3, $CaZrO_3$, Nb_2O_5 (Curie peak suppressors) and CuO, Li_2O, PbO (fluxes) are used with $BaTiO_3$ [14-16].

However, detailed information relating to the behavior of such complex mixtures during sintering in reducing/inert atmosphere (so that nickel electrodes can be used) is lacking and hence such process warrant detailed studies.

N. Halder et. al have investigated three basic composition viz. ($BaTiO3+0.65\%Li_2B_4O_7$; $BaTiO_3+0.65\%Li_2B_4O_7+0.40\%Bi_2O_3$; $BaTiO_3+0.65\%Li_2B_4O_7+0.40\%Bi_2O_3+0.40\%MnO_2$) and studied the effect of sintering atmosphere containing different percentages of oxygen and argon on various process parameters like bulk densities, dielectric constant and phase transformations [4].

It is very difficult for complexes like $BaTiO_3$-MgO (MnO_2)-Re_2O_3 (where Re represents the rare earth elements with smaller ionic radius) to satisfy the R characteristics ($\Delta C/C=\pm 15\%$) when the temperature is above 130°C as T_c =125°C for $BaTiO_3$. This complication can be overcome by adding smaller ionic radius rare earth elements, such as Sc, Tm, Er and Yb, because they shift the Curie temperature to higher temperatures [17].

Similar investigation was done by Shen wang et. al[18] studying the effect of Yb/Mg co-doping on the electrical properties and microstructure of $BaTiO_3$ ceramics, sintered under oxidizing, reducing and annealed atmospheric conditions. The suppression of the solubility, of the acceptor ions in $BaTiO_3$ under the annealed and reducing conditions was indicated by XRD analyses.

2.3 Summary of Literature:

Following are the key points of the literature survey;

a) Several mechanisms can be employed for the synthesis of $BaTiO_3$ nano-powders.
b) To get the enhanced efficiency from $BaTiO_3$ ceramics at various temperature ranges, they are required to be doped.
c) Without sacrificing densification, lithium tetraborate (as flux) and bismuth oxide (as flux and Curie peak suppressor) doped $BaTiO_3$ based capacitor compositions, can be fired in an inert (argon) atmosphere.
d) Addition of a small amount of MnO_2 in the compositions, can suppress the increase of both the dissipation factor and dielectric constant of the samples containing Bi_2O_3 when sintered in inert atmosphere.
e) In case of Yb/Mg co-doping there is suppression of solubilities, of the acceptor ions when fired in reducing atmospheres.
f) The formation of n-type electronic defects in case of bismuth containing composition without MnO_2 leads to a dramatic increase in both the DF and K values when firing is done in atmospheres containing < 25% O_2, the annihilation of the defects and inhibition of the dramatic increase of both the DF and K values of bismuth containing samples can be achieved by doping with Mn^{2+} ions which is well-known acceptor.

2.4 Objective of present studies:

Nano-structured $BaTiO_3$ has significant importance for the preparation of MLCC, which is preferably sintered at Ar and/or N_2 atmosphere during fabrication. Hence, systematic synthesis of $BaTiO_3$ nano-powders and their sintering study at different atmosphere is worthwhile. In this backdrop, the following objective needs to explore;

a) Synthesis of $BaTiO_3$ nano-powders through combined wet chemical and calcination technique.
b) Sintering study at different atmosphere (Air, Ar and N_2) with different heating schedule.
c) Microstructure Study of nano-structured $BaTiO_3$.

Chapter 3

Experimental Work

3.1 Synthesis of Barium Titanate ($BaTiO_3$)

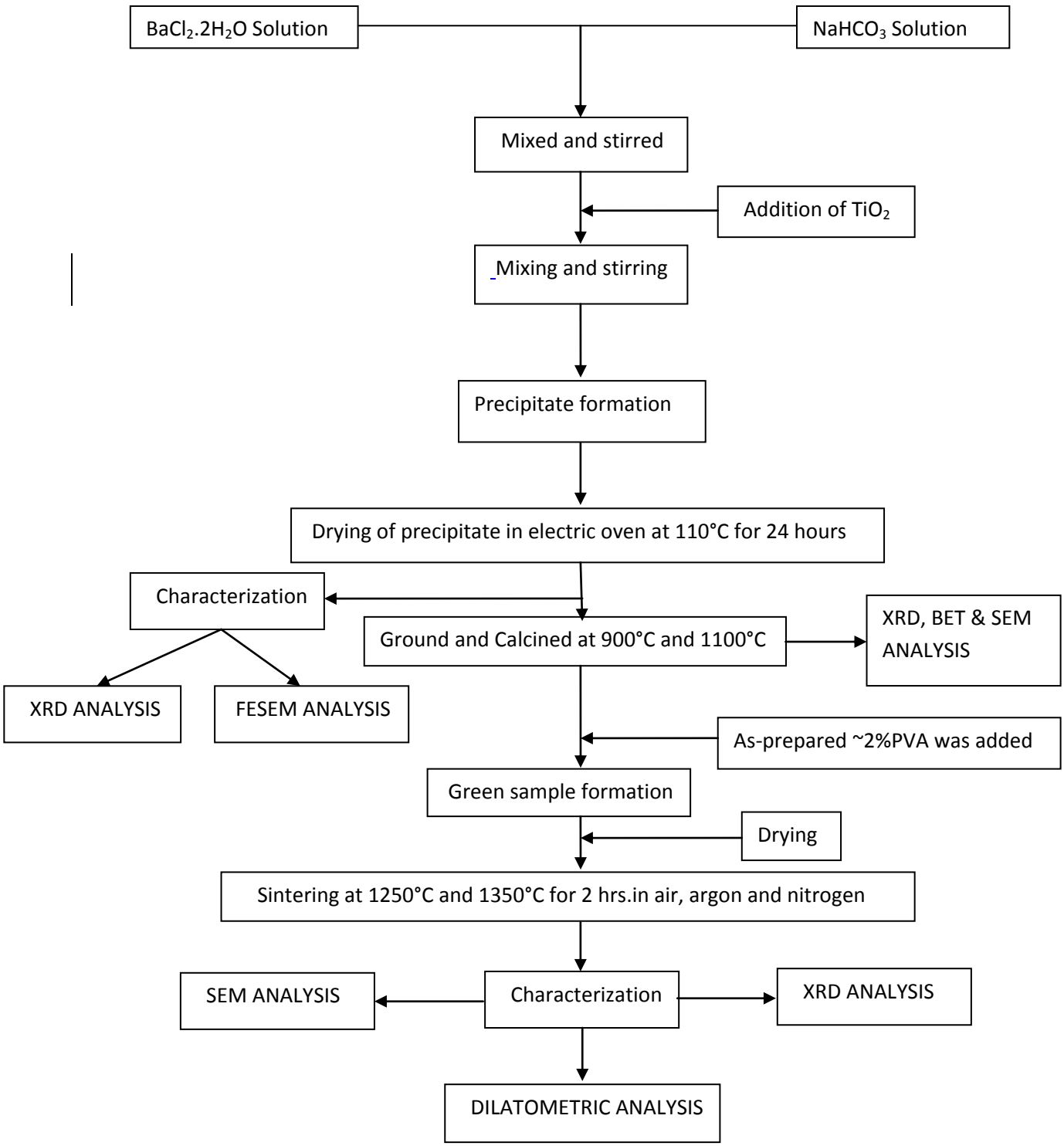


Fig. 3.1 *Flow Diagram of the Procedure*

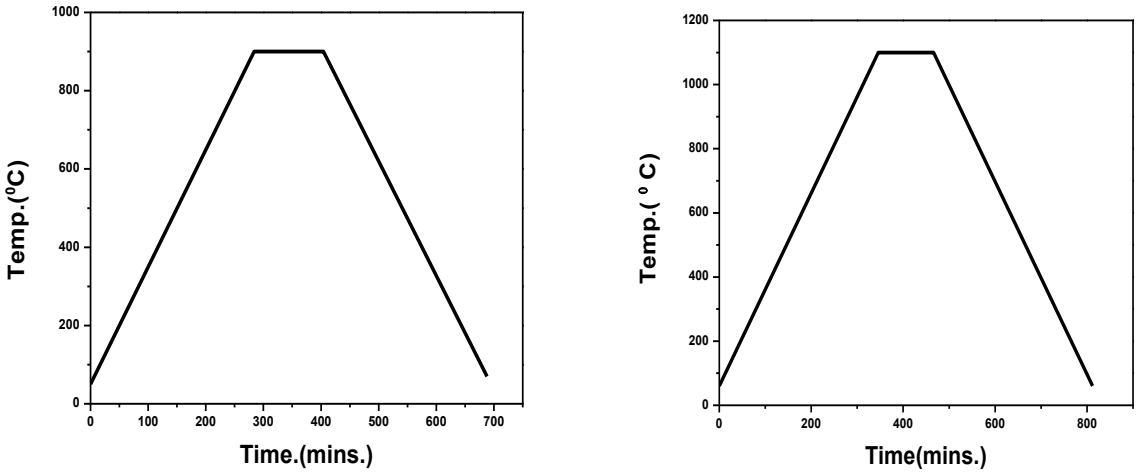
3.1.1 Powder Preparation:

Solution of required amount of Barium Chloride dihydrate crystal ($BaCl_2.2H_2O$) and that of Sodium Bicarbonate ($NaHCO_3$), in distilled water, were prepared in separate beakers, by using magnetic stirrer till the solution became transparent. After that $NaHCO_3$ solution was added drop wise and slowly to the $BaCl_2.2H_2O$ solution, and required amount of Titanium Dioxide (TiO_2) was added to the mix and stirred for 45mins.Then the beaker covered with a petri-dish, was left undisturbed for 24hours, at room temperature for precipitation to occur.

The precipitate thus formed was subsequently washed several times with distilled water and the drained water was tested for the presence of NaCl (by product of the reaction), using aqueous solution of Silver Nitrate ($AgNO_3$).

So precipitate was washed till the whitening of $AgNO_3$ solution stops. Finally, the precipitate was washed with 2-Propanol, through the wattman (41) filter paper and then kept in oven at 110°C for 24hours, for drying. The sample was then scrapped out from the petri-dish and weighed. The dried samples were ground and calcined at 900°C and1100°C for 2hours.

- ***Powder calcinations profile:***



(A) (B)

Fig.3.2 For calcination at (A)900°C and (B)1100°C for 2 hours.

3.1.2 Powder Characterization:

X-ray diffraction patterns were obtained using X-ray diffractometer Phillips PANalytical (Model: PW 1830diffractometer, Netherland) with Cu Kα radiation. The pattern was obtained in the 2θ range from 20^{o}-90^{o} and the scan time range was 15mins to 58mins. Nitrogen physisorption was used to determine the surface area of the materials at the temperature of liquid nitrogen (-196ºC) in a (Quantachrome, USA); prior to analysis, the samples were degasified for 3 hours at 300ºC. To study the surface morphology of the samples, the powders were subjected to Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FESEM).

3.2 Preparation of binder and green specimens:

Initially, during pressing of powder (with force 4.5 Ton and dwell time 90 secs.) without any binder added, at the time of ejection, pellets started disintegrating at the edges. So, PVA (poly vinyl alcohol) was used for the binding purpose to provide green body strength. Prior to use of the PVA binder, 1.906gms of PVA granules was added slowly to the water kept on magnetic stirrer. Simultaneous, heating and stirring was carried out for around 45 mins. Then, with the formation of a clear solution, the stirring and heating was stopped. The solution was then stored in a bottle for further application.

3.3 Sintering behavior of green compacts

Powder calcined at 1100°C was mixed with small amount of previously prepared PVA solution. Then the mix was left for drying. Powder was then divided into 3 parts and pressed in a rectangular die (with force of 4.5 Ton and dwell time 90 secs.).

3.3.1 Characterization of Sintered Specimens:

The dilatometric study was carried out with the help of NETZSCH DIL 402C instrument. The samples were analysed in the presence of 100%air, 100%nitrogen and 100% argon environments, with a heating rate of 10°C/min. in the temperature range of 30°C to 1250°C and 30°C to 1350°C after that keeping the samples in isothermal condition for 2 hours. The specimen did not stick with alumina holder.

X-ray diffraction patterns were obtained using X-ray diffractometer Phillips PANalytical (Model: PW 1830diffractometer, Netherland) with Cu Kα radiation. The pattern was obtained in the 2θ range from 20^{o}-90^{o} and the scan time was 58mins. To study the surface morphology of the samples, the powders were subjected to Scanning Electron Microscopy.

Chapter 4

Results And Discussions

This chapter illustrates the relevant research data on BaTiO3 nano-powders and their sintering characterization in different atmosphere.

4.1 Phase analysis of synthesized nano-powders of $BaTiO_3$:

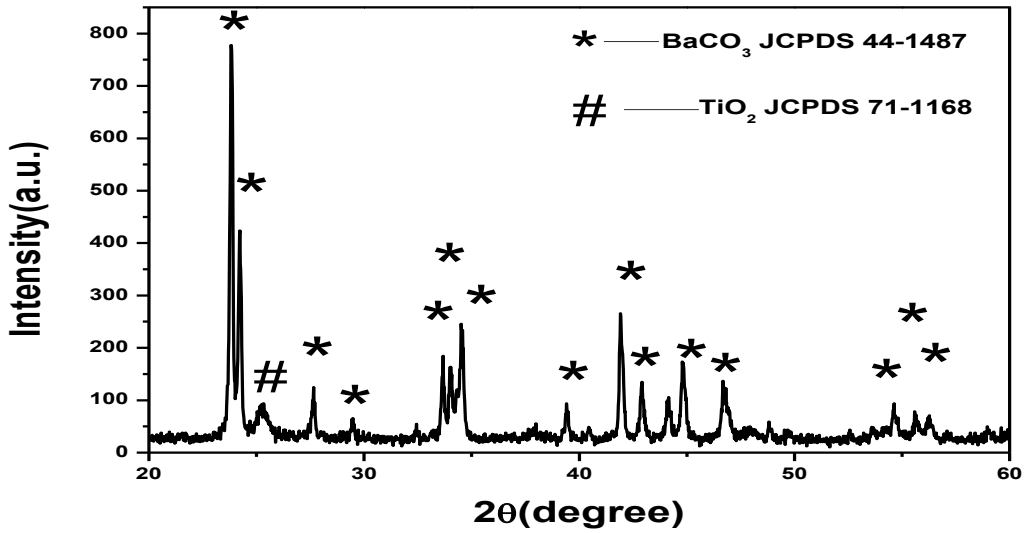


Fig.4.1 XRD pattern of $BaCO_3$ and TiO_2 precursor powder mix.

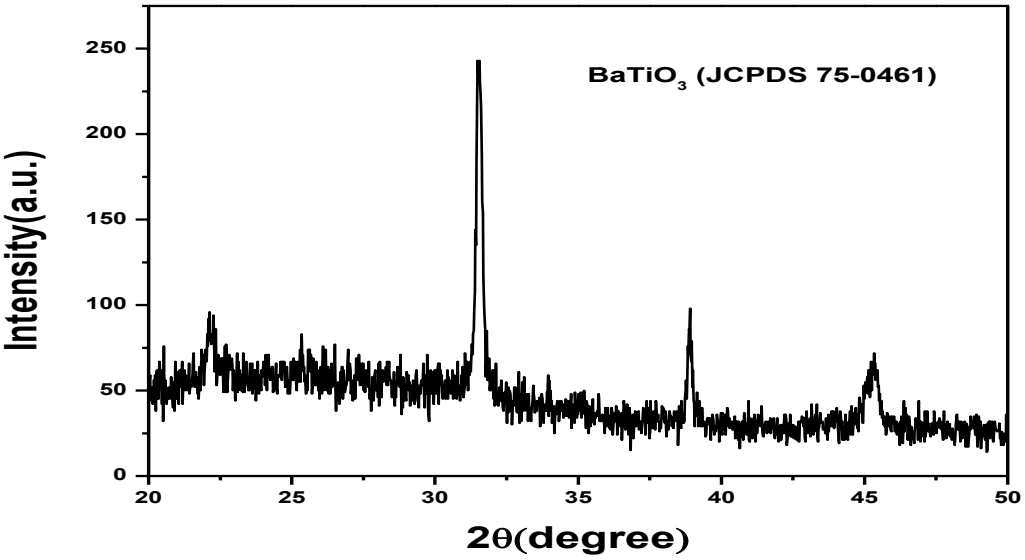


Fig.4.2 XRD pattern of $BaTiO_3$ nano-powder calcined at 900°C for 2hours.

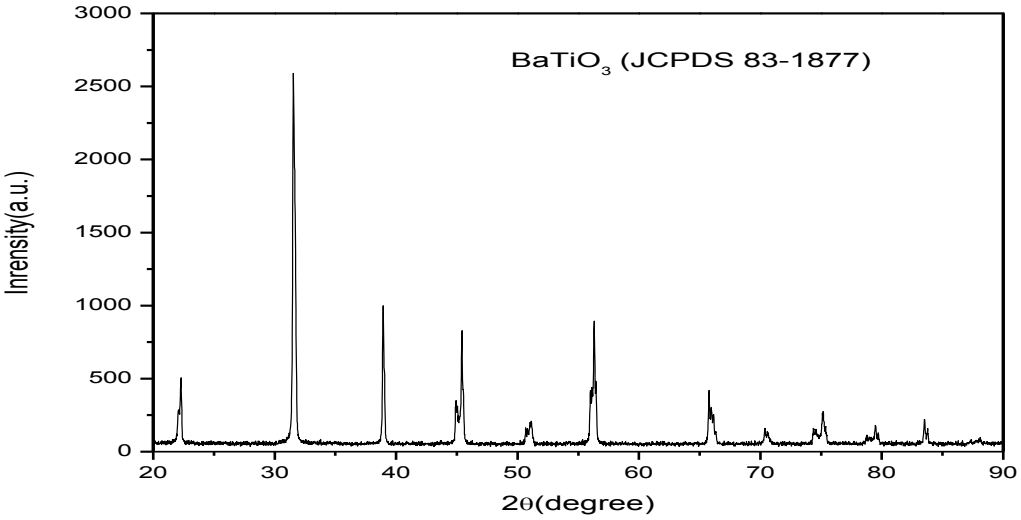


Fig.4.3 XRD pattern of $BaTiO_3$ nano-powder calcined at 1100°C for 2hours.

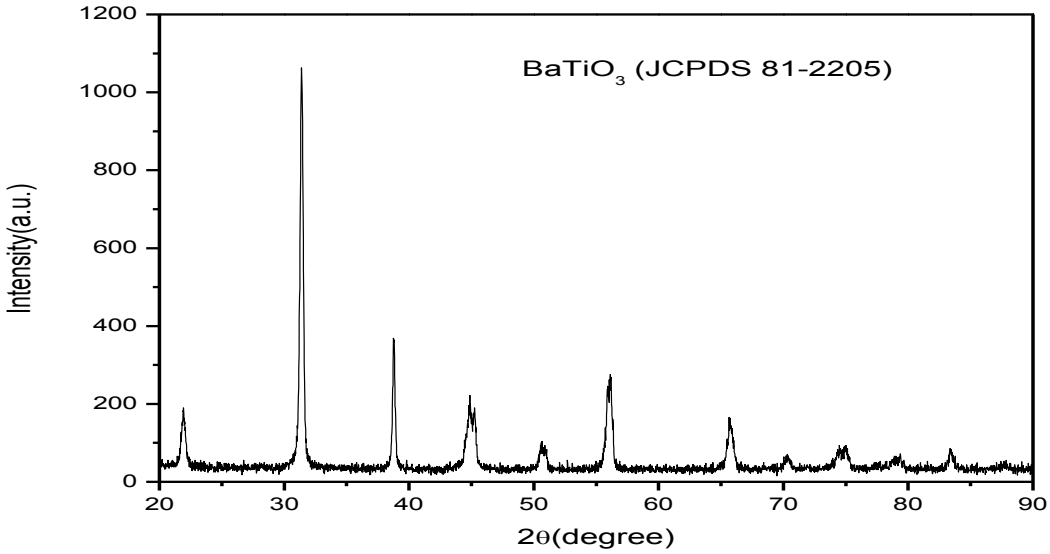


Fig.4.4 XRD pattern of $BaTiO_3$ nano-powder sintered at 1250°C for 2hours in air.

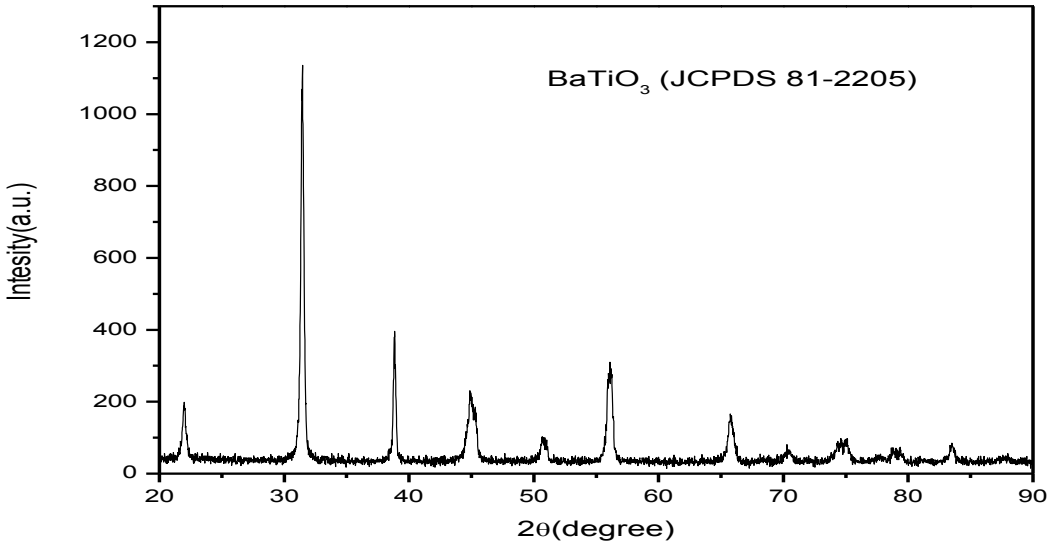


Fig.4.5 XRD pattern of $BaTiO_3$ nano-powder sintered at 1250°C for 2hours in argon.

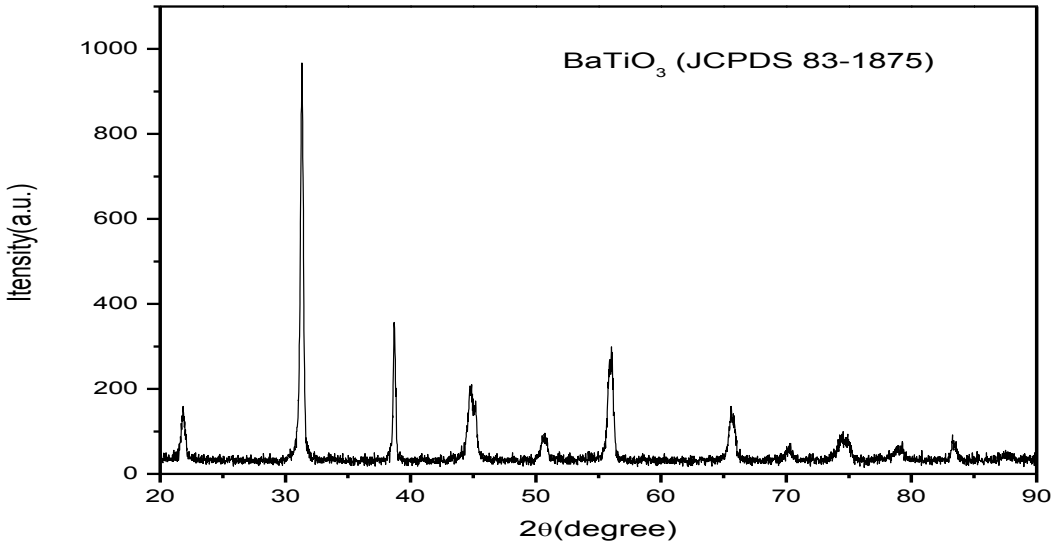


Fig.4.6 XRD pattern of $BaTiO_3$ nano-powder sintered at 1250°C for 2hours in nitrogen.

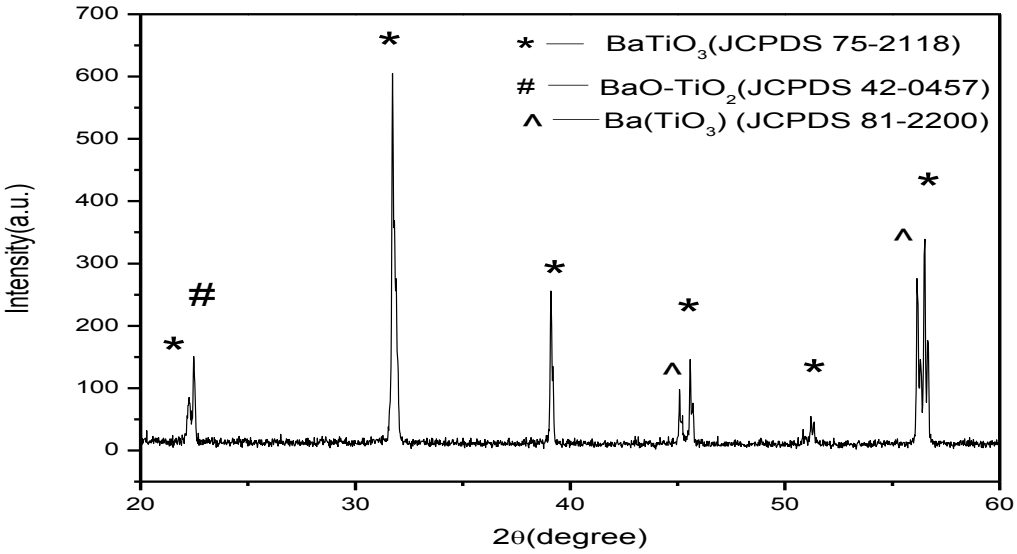
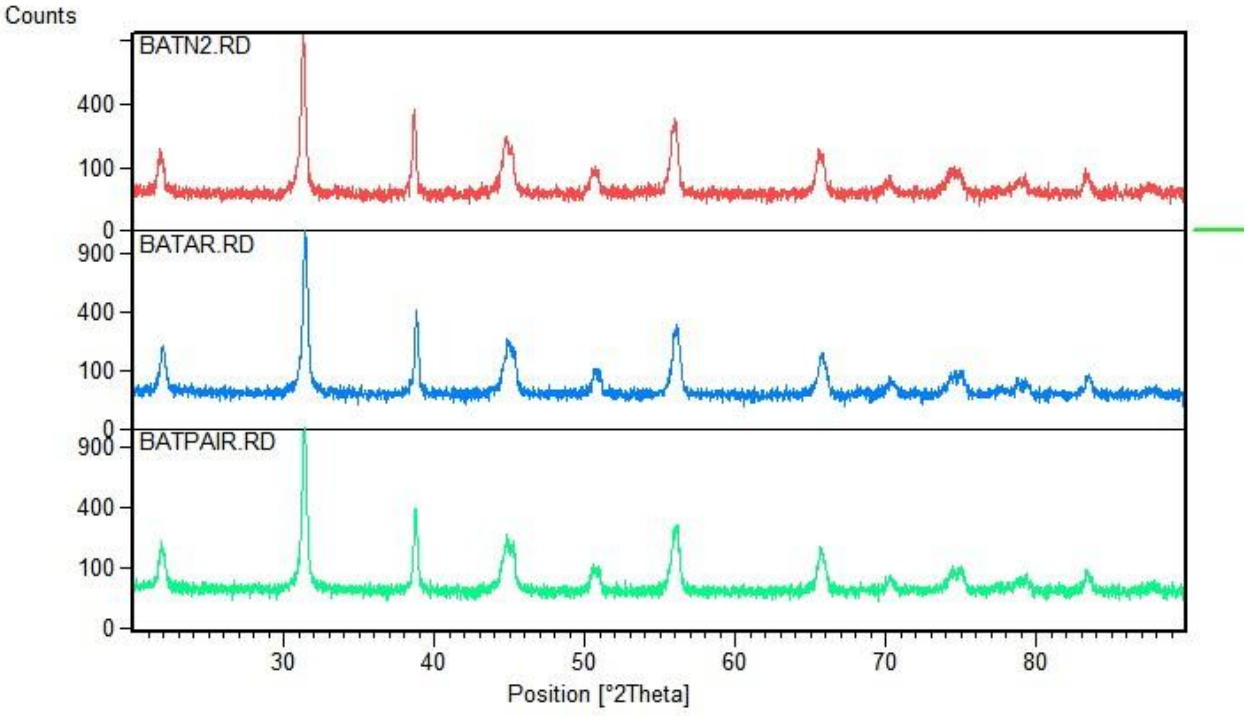
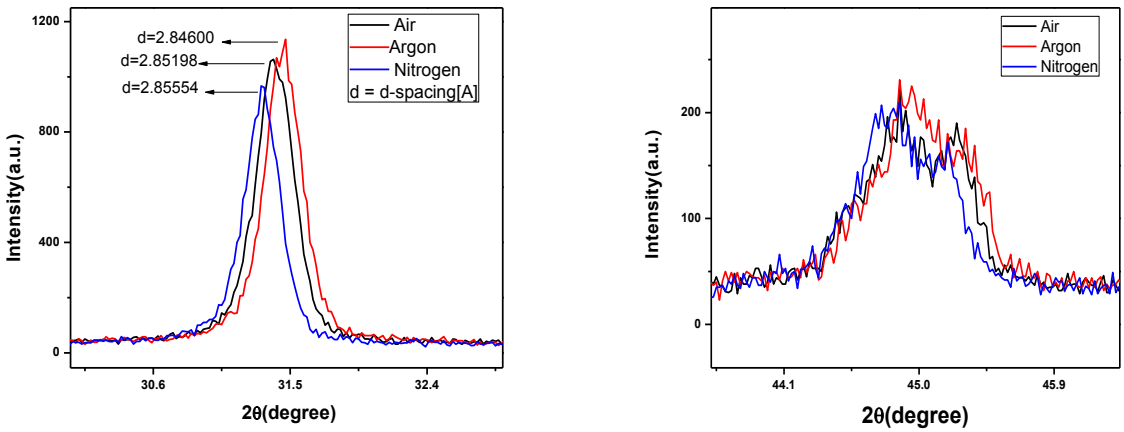


Fig.4.7 XRD pattern of $BaTiO_3$ nano-powder sintered at 1350°C for 2hours in nitrogen.

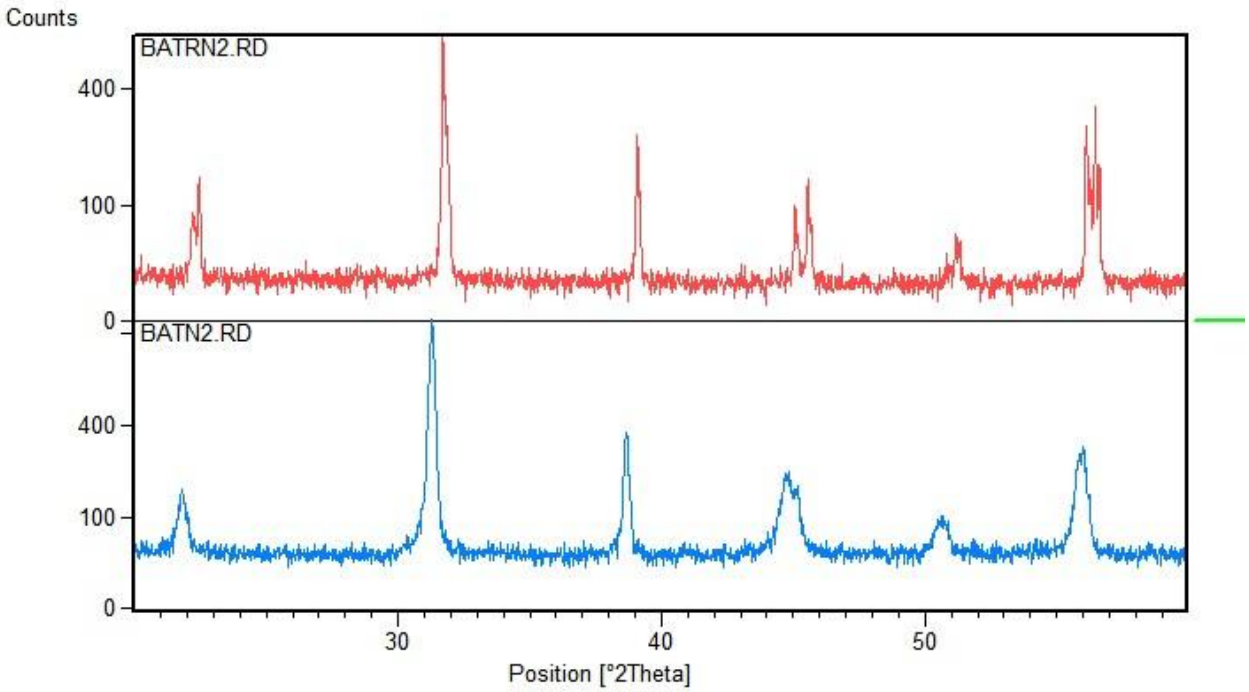


(A)



(B)

Fig.4.8 (A) and (B) XRD pattern for sintered $BaTiO_3$ in different atmospheres at 1250°C.



(A)

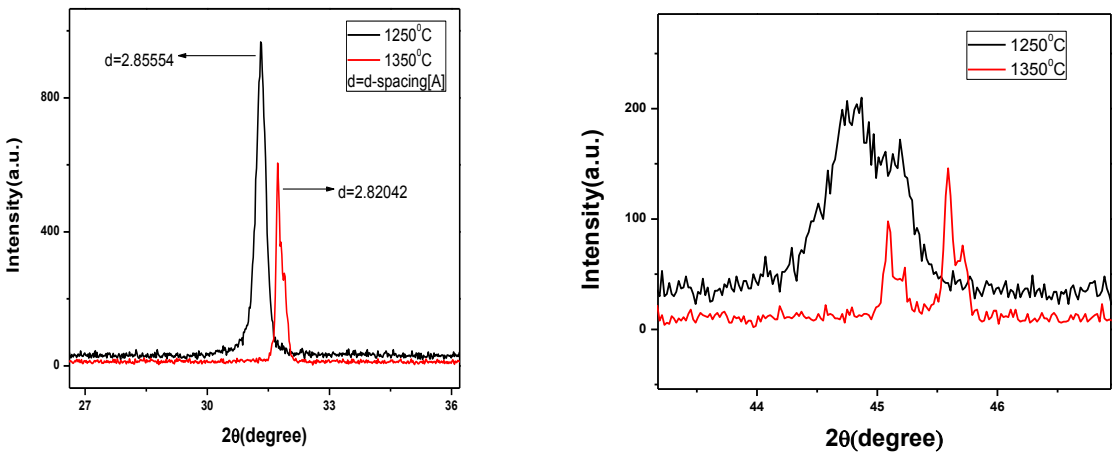


Fig.4.9 (A) and (B)XRD pattern for sintered $BaTiO_3$ in nitrogen atmosphere at 1250°C and 1350°C

(B)

Table 4.1

Sample	BAT1100 (Powder)	BATPAIR (1250°C)	BATAR (1250°C)	BATN2 (1250°C)	BATRN2 (1350°C)
Crystallite size(nm)	82.6	61.12	40.77	45.86	91.8
Crystal structure	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal

Crystallite size and Crystal structure from XRD analysis

4.2 Relative Density:

Table 4.2

Environ. / Temp.	Air	Argon	Nitrogen
1250°C	0.925	0.887	0.92
1350°C	0.929	0.892	0.927

Relative density of specimen sintered in air, argon and nitrogen at 1250°C and 1350°C.

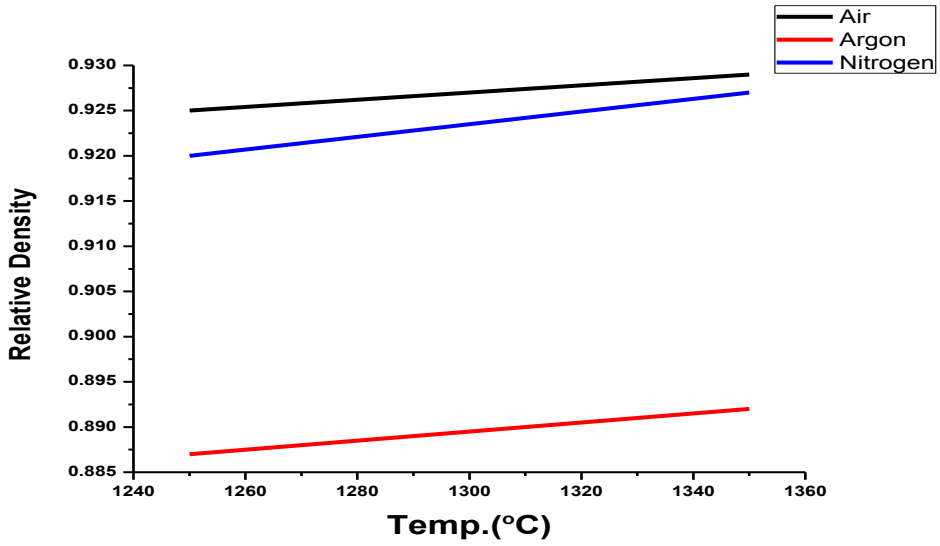


Fig.4.10 Relative density Vs Temperature curve in air, argon and nitrogen.

4.3 Surface Area

Using Brunauer-Emmett-Teller (BET), the surface area of the sample was determined. Equivalent particle size can be determined from the measured surface area using the equation:

$$D_{BET} = \frac{6000}{\rho \, X \, S_{BET}}$$

where,

I. D_{BET} (nm) is the average particle size

II. S_{BET} is the surface area expressed in m^2/g and

III. ρ is the theoretical density of $BaTiO_3$ expressed in g/cc.

It was found that for $BaTiO_3$ nano-powder calcined at 900°C for 2hours, S_{BET} value equals to 7.295 m^2/g , so D_{BET} calculated equals to 137nm.

While for $BaTiO_3$ nano-powder calcined at 1100°C for 2hours, S_{BET} value equals to 3.284 m^2/g , so D_{BET} calculated equals to 303nm.

4.4 Surface morphology analysis:

SEM Analysis:

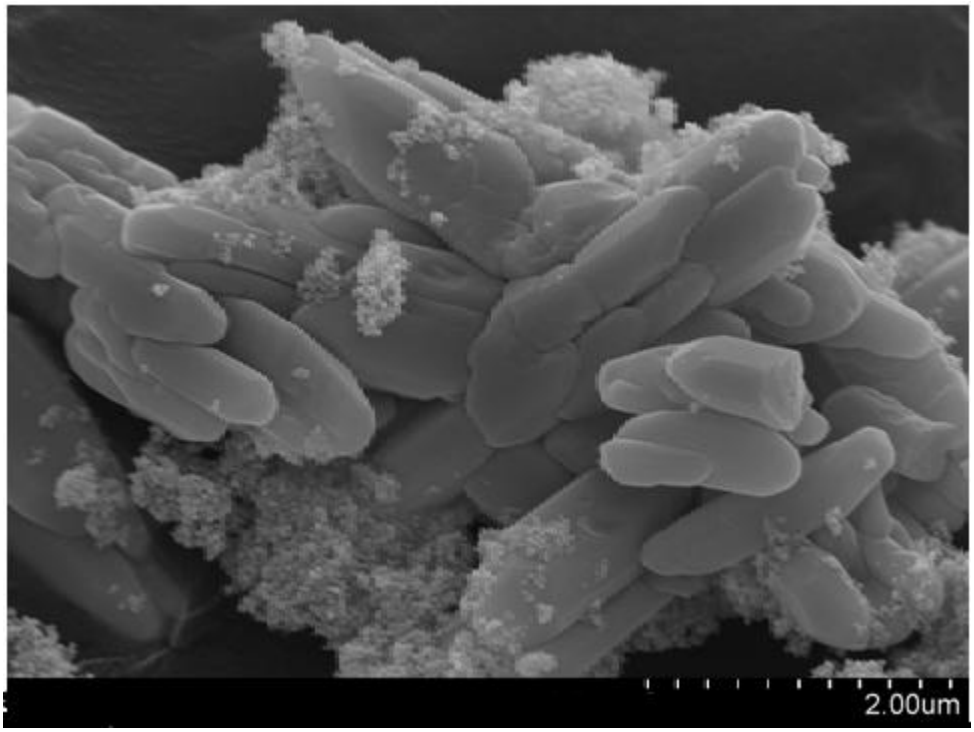


Fig.4.11 FESEM image of $BaCO_3$ and TiO_2 mix precursors

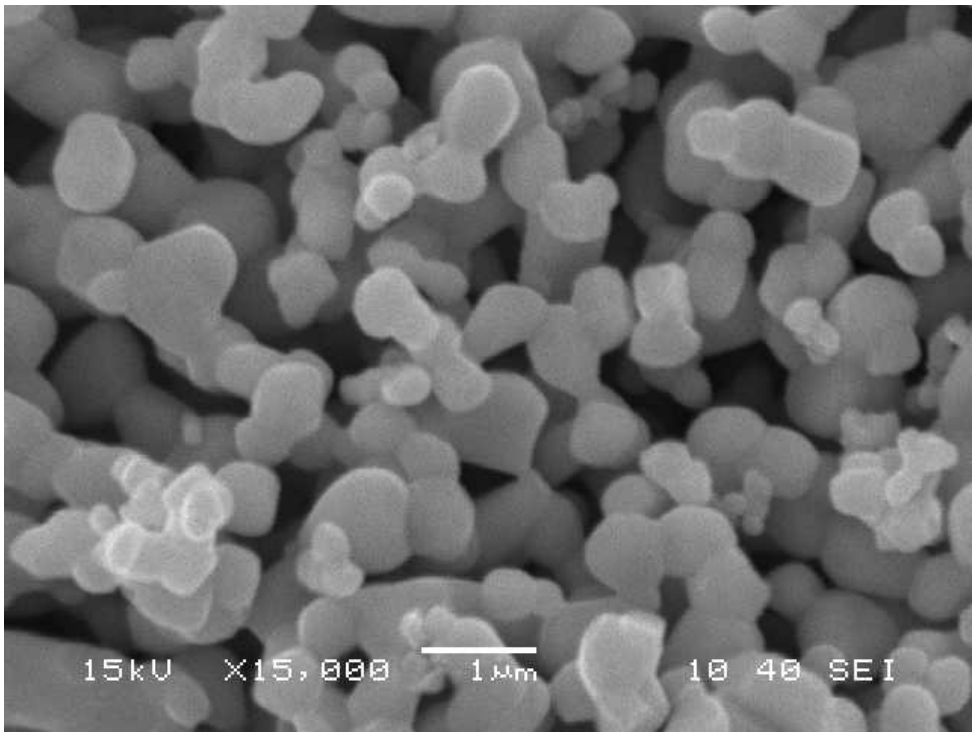


Fig.4.12 $BaTiO_3$ nano-powder calcined at 1100°C for 2hours.

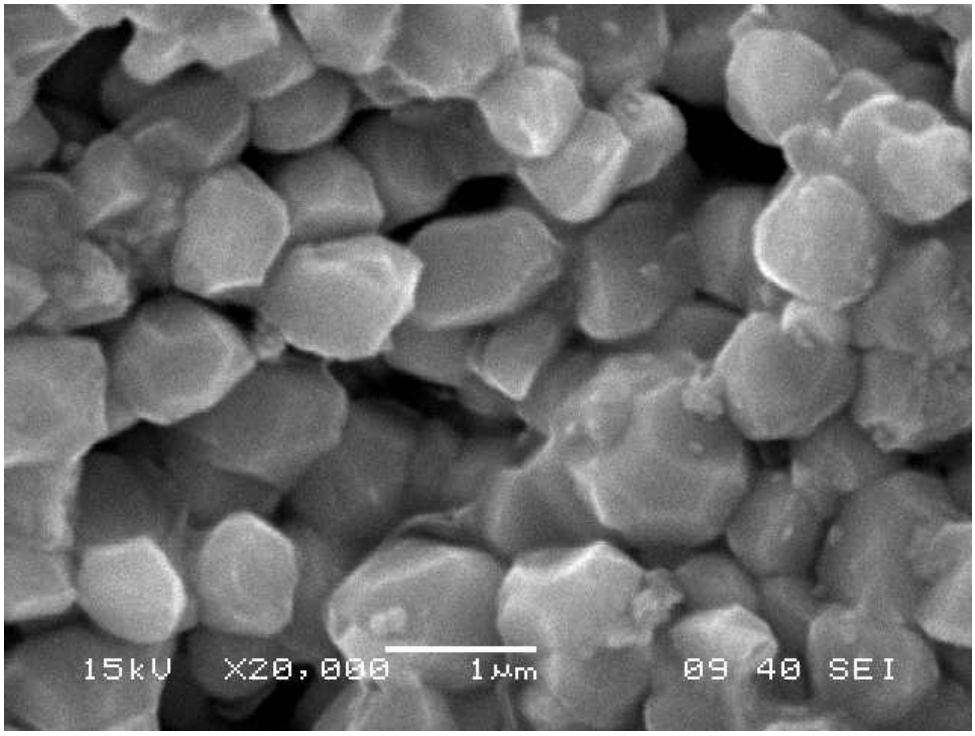


Fig.4.13 Green specimen of $BaTiO_3$ nano-powder sintered at 1250°C for 2hours in air.

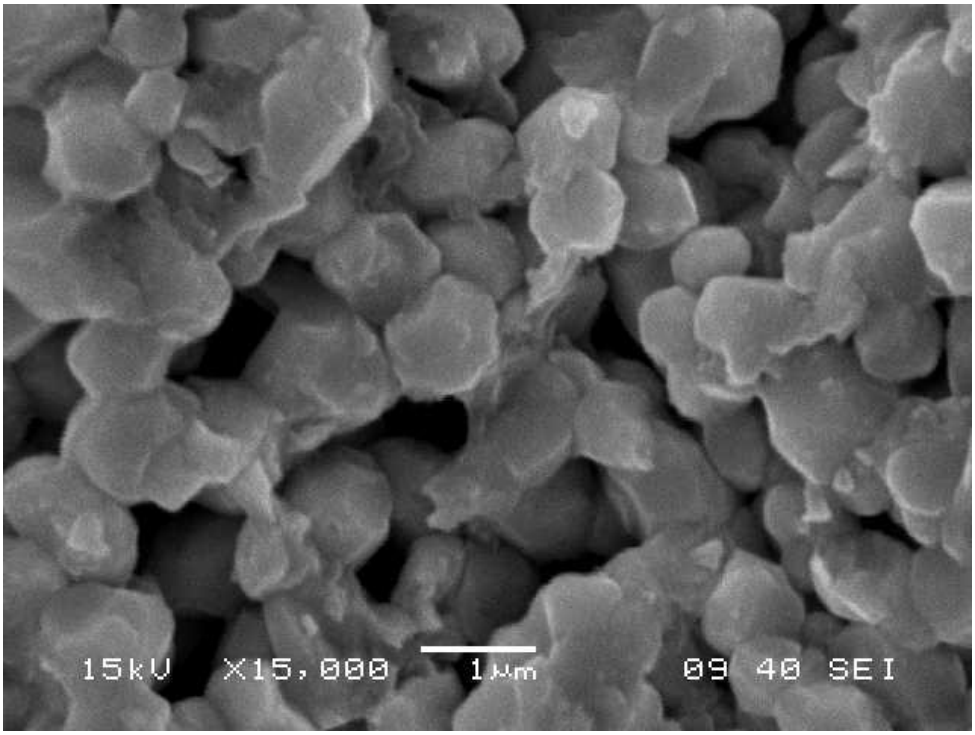


Fig.4.14 Green specimen of $BaTiO_3$ nano-powder sintered at 1250°C for 2hours in nitrogen.

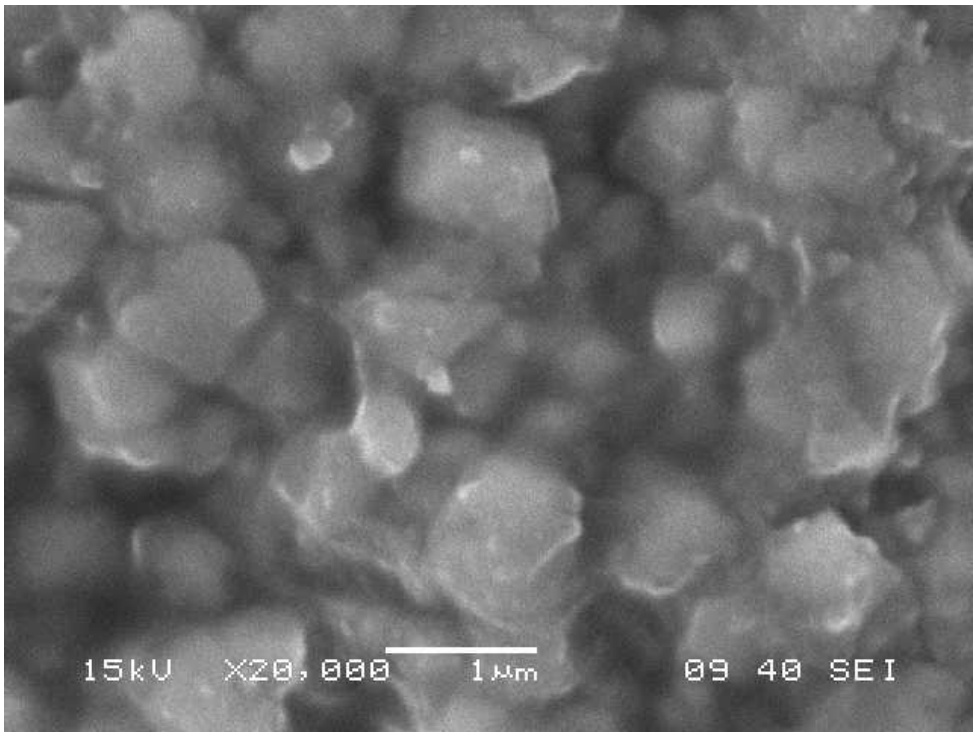


Fig.4.15 Green specimen of $BaTiO_3$ nano-powder sintered at 1250°C for 2hours in argon.

4.5 Dilatometric Analysis of green specimen of $BaTiO_3$ nano-powder:

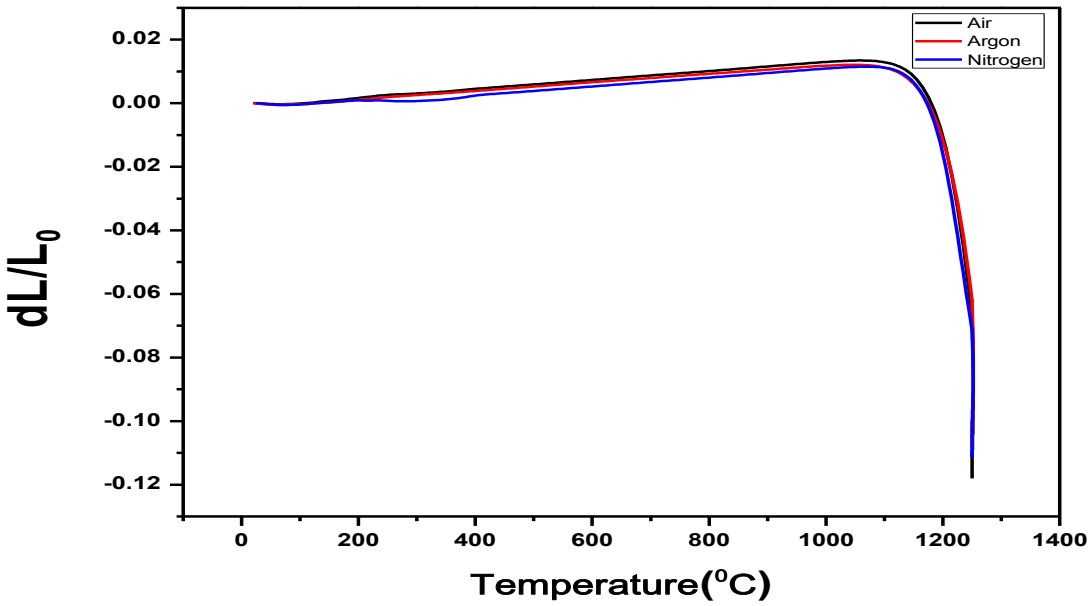


Fig. 4.16

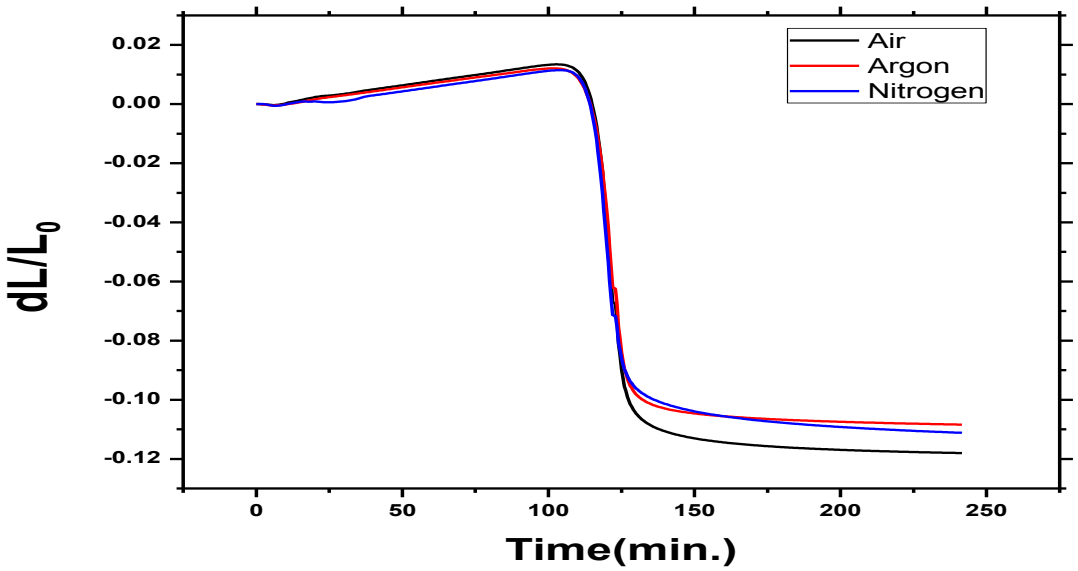


Fig. 4.17

Dilatometric curve for green specimen of $BaTiO_3$ nano-powder sintered at 1250° for 2hours in air, argon and nitrogen.

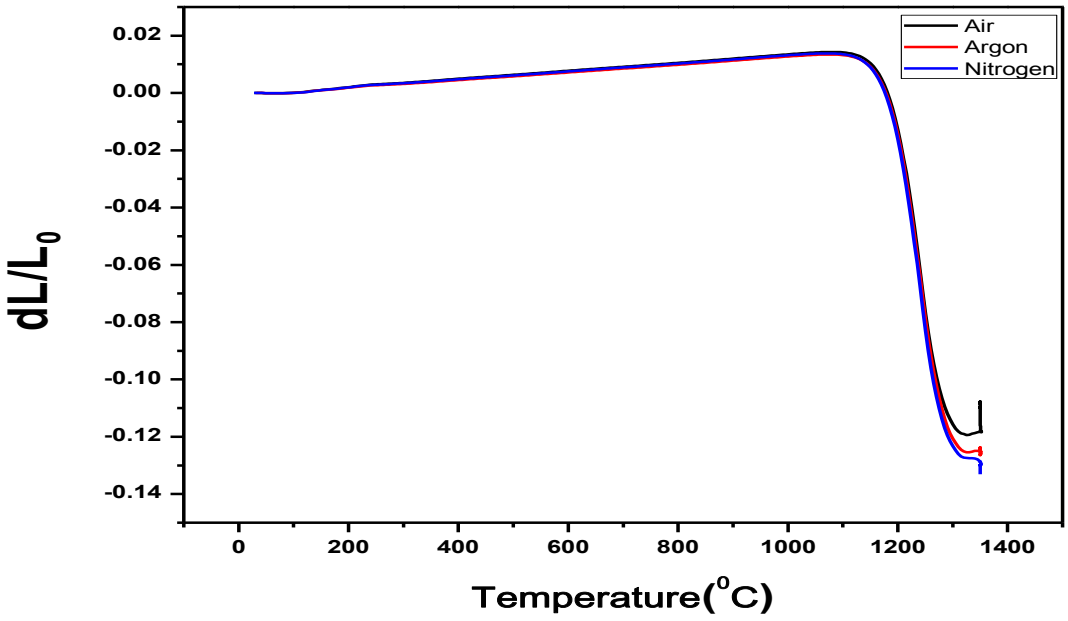


Fig. 4.18

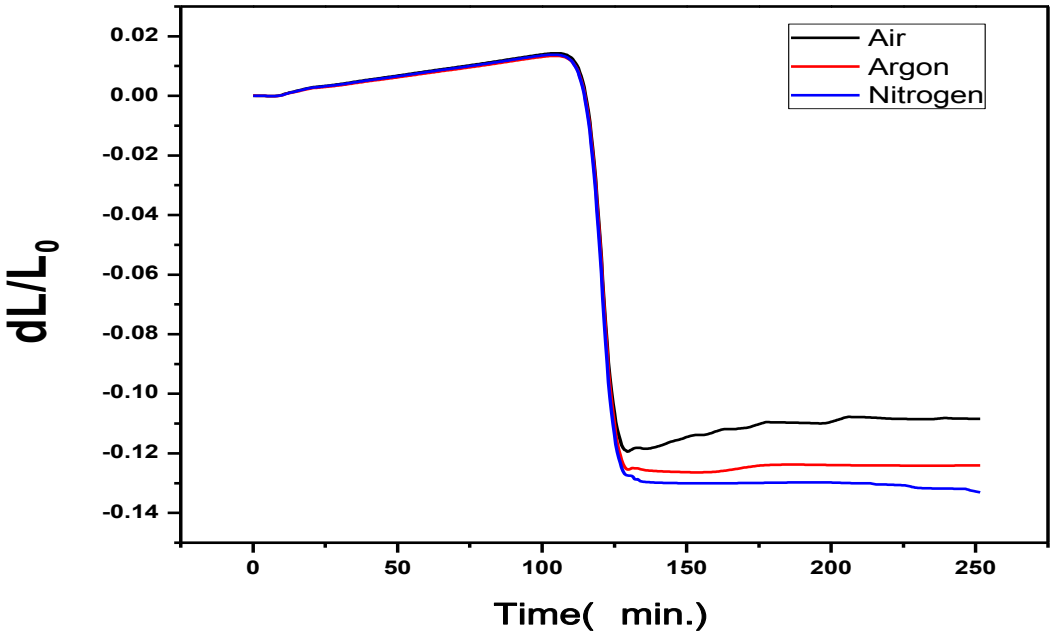


Fig. 4.19

Dilatometric curve for green specimen of $BaTiO_3$ nano-powder sintered at 1350° for 2hours in air, argon and nitrogen.

Chapter 5

Conclusions

Conclusions:

1. Low temperature 950^{o}C develops 130nm $BaTiO_3$ nanoparticles with having small amount of $BaCO_3$ impurities and low c/a ratio.
2. Particle increases up to 300nm with increasing temperature up to 1100^{o}C
3. Pure, high crystalline, high c/a ratio was obtained at 1100^{o}C temperature.
4. Relative density of consolidate $BaTiO_3$ nanopowders in air, nitrogen and argon were densified up to 92.5%, 91.8% and 88.5%, respectively.
5. Lattice parameter and d-spacing of $BaTiO_3$ are changing with sintering atmosphere.

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